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Metal-insulator transition at a depleted LaAlO₃/SrTiO₃ interface: Evidence for charge transfer induced by SrTiO₃ phase transitions

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Two anomalous bias dependent resistive peaks induced by the SrTiO₃ structural phase transitions at 55 and 110 K were observed in a LaAlO₃/SrTiO₃ and Nb:SrTiO₃ rectifying junction when the LaAlO₃/SrTiO₃ was depleted under reverse bias. At these transition temperatures, the barrier between LaAlO₃/SrTiO₃ and Nb:SrTiO₃ showed abrupt changes in the tunneling energy under forward bias. The peak at 110 K was an insulator-metal phase transition while the peak at 55 K was a metal-insulator one. We propose that the phase transitions of the SrTiO₃ substrate influence the charge transfer to the LaAlO₃/SrTiO₃ layer, giving rise to these anomalous resistive peaks. © *2011 American Institute of Physics*. [doi:10.1063/1.3656703]

Oxides exhibit many exciting properties, such as superconductivity,[1] colossal magnetoresistance,[2] ferroelectricity,[3] and multiferroicity,[4] which are the basis for oxide electronics. These properties were further enhanced by the observation of quasi two dimensional electron gas (Q2DEG) in a LaAlO₃/SrTiO₃ heterointerface by Ohtomo and Hwang,[5] which was a remarkable result as the conducting layer produced was at the interface between two insulators. In addition to the high carrier density and mobility, the LaAlO₃/SrTiO₃ interface features many fascinating properties such as superconductivity[6] and even magnetism.[7] Nevertheless, some possible applications of this Q2DEG for all-oxide high mobility field effect transistors have been proposed on account of the very large charge mobility in this Q2DEG layer. A detailed understanding of the nature of this metallic interface is required for fully exploiting any device technology based on this phenomenon.

Although several fundamental mechanisms underlying this phenomenon were proposed including electronic reconstruction,[8] cationic diffusion,[9] band bending,[10] and oxygen vacancy,[11] the origin of the metallic interface is still unclear. For example, the polarization catastrophe model would require a transfer of about 0.5 electrons per LaAlO₃ unit cell to the SrTiO₃ resulting in a Q2DEG of 3.2×10^{14} cm^{-2}. Experimentally, however, only one tenth of this carrier density has been reported.[12] The imperfect lattice match of SrTiO₃ (cubic) with LaAlO₃ (orthorhombic) is likely to create an interface strain which may account for this discrepancy. To validate this idea, we can look at the effect of the phase transitions at 110 and 55 K of SrTiO₃ which will induce a strain/polarization at the LaAlO₃/SrTiO₃ interface and possibly result in charge transfer variation to this interface. To be able to detect small variations in the charge transfer, the interface need to be depleted so that it has the least number of carriers.

A recent paper[13] exploring the device potential of the LaAlO₃/SrTiO₃ interfaces with metal electrodes such as copper showed a rectifying junction. In the reverse bias a very large breakdown voltage was observed though this was not seen in all the devices, possibly due to local defects. The most significant piece of this work is the observation of a complete depletion of the charges when the device is reverse biased, creating an insulating channel at the interface. A recent paper by Bark *et al.*[14] showed that the charge transfer can be influenced by the lattice mismatch between LaAlO₃ and SrTiO₃, which can be induced by preparing this LaAlO₃/SrTiO₃ interface on different substrates. It was shown that the carrier density is decreased exponentially by very slight compressive strain. In fact, SrTiO₃ itself experiences various structural phase transitions as function of temperatures, which can provide different tensile or compressive strain to the interface. In this letter, we show a strong coupling between the structural phase transitions of SrTiO₃ and the transport property of the Q2DEG in Q2DEG/Nb:SrTiO₃ junctions, which gives evidence for charge transfer variations from the LaAlO₃ layer to the LaAlO₃/SrTiO₃ interface.

Ten unit cells of LaAlO₃ layers were fabricated by pulsed laser deposition technique, on TiO2-terminated (001)-oriented SrTiO₃ substrate (Fig. 1(a)), with step flow surfaces achieved by combining chemical and thermal treatment.[15] Prior to the LaAlO₃ deposition part of the surface was masked by a LaAlO₃ crystal and the unmasked surface was monitored by reflection high energy electron diffraction (RHEED) during the growth of LaAlO₃, as shown in Fig. 1(b), which indicates 2D layer-by-layer growth of the LaAlO₃ layers. Immediately after, the mask was removed and a new mask was introduced to cover part of the region coated with LaAlO₃. A Nb-doped SrTiO₃ (0.5 wt%) layer was then deposited to a thickness of 100 nm, with a 5 mm² overlap area with the LaAlO₃ deposited earlier. During the two deposition processes, the temperature of the substrate was kept at 700 °C, and at an oxygen pressure of $\sim 10^{-2}$ Torr. As electrodes, four copper pads were deposited on Nb:SrTiO₃ and LaAlO₃, respectively. Figure 1(c) shows a sketch of our device where Nb:SrTiO₃ is directly contacted to the LaAlO₃/SrTiO₃ interface. In order to guarantee the
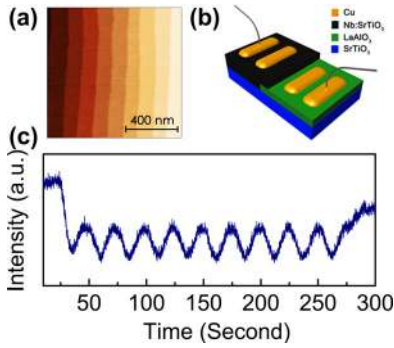
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FIG. 1. (Color online) (a) AFM image of SrTiO$_3$ substrate after buffered hydrogen fluoride treatment showing step flow surface. (b) RHEED intensity monitored during growth of 10 unit cells of LaAlO$_3$ on an SrTiO$_3$ substrate. (c) Schematic structure of the device.

main junction is between Nb:SrTiO$_3$ and Q2DEG, a soft breakdown was applied on the two Cu electrodes on LaAlO$_3$. Independent measurements of the resistivity of the Cu-Q2DEG-Cu and the Cu-Nb:SrTiO$_3$-Cu contacts showed Ohmic-like behavior, as depicted in Figs. 2(a) and 2(b). The contact resistances between the Cu electrode and Q2DEG or Nb:SrTiO$_3$ were ~2 kΩ, which were determined by the current-voltage measurements between two copper electrodes with a distance of 1 mm at the ambient temperature. The temperature dependence of these contact resistance contributions were smaller than those for the Nb:SrTiO$_3$/Q2DEG junction under both forward and backward biases and hence can be neglected in our discussions. Based on the conventional semiconductor theory, the transport property of a junction is determined by the band structures of the two materials. The strong polarity dependent changes in the current-voltage curves strongly suggests the formation of a Schottky barrier at the Nb:SrTiO$_3$/Q2DEG interface which enables us to deplete the conducting channel. The LaAlO$_3$ edge created by masking is actually a graded edge and is not abrupt. The region having Q2DEG has an LaAlO$_3$ layer thicker more than 4 unit cells for the Nb:SrTiO$_3$ to make contact with the channel. In the region where the Nb:SrTiO$_3$ makes excellent contact with the channel there is no Q2DEG. So the contact which most likely will be a tunnelling, Schottky-like contact will occur at some intermediate LaAlO$_3$ thickness. While the forward transport was limited by a tunnel barrier formation at the Nb:SrTiO$_3$/Q2DEG junc-
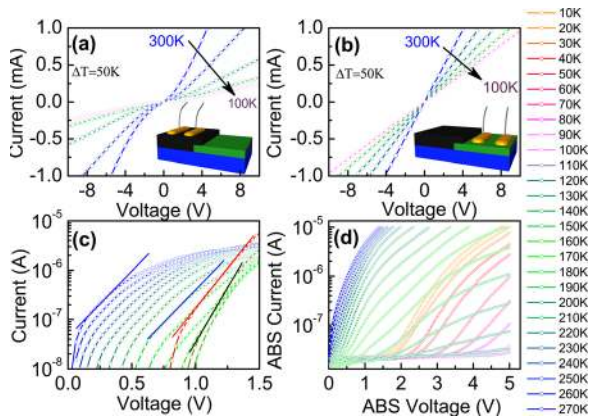
tion, the reverse characteristics showed dramatic resistance peaks which can be associated with the phase transitions in SrTiO$_3$. The devices were reproducible and so were the phase transition and barrier effects on the transport properties.

Figures 2(c) and 2(d) shows current-voltage (I-V) data of the Q2DEG/Nb:SrTiO$_3$ junction, measured in the temperature range from 270 to 5 K where a positive bias was applied on Nb:SrTiO$_3$. The Q2DEG/Nb:SrTiO$_3$ junction exhibits rectifying behavior. Above 150 K, the resistance versus temperature shows a semiconducting behavior at low voltages which transforms into a metallic behavior at about 1.7 V. The constant slope of semilog I-V curves with the variation of temperature indicates that the tunneling current dominates.[16] The tunneling current can be described by $J = J_s \exp(qV/E_{00})$, where $E_{00} = qh/4\pi(N_D/m^*\epsilon_0\epsilon)^{1/2}$ is the energy for tunneling, J_s is the saturation current, N_D is the donor concentration, m^* is the effective mass, and q is the electron charge. From this, the energy for tunneling E_{00} of 0.1, 0.06 and 0.07 eV are found (Fig. 3(b)) to be constant in three different temperature regimes of 270−110, 110−55, and below 55 K, respectively. For the temperature ranges of 110−55 and below 55 K, the I-V curves are temperature independent for both the slope and the saturation current. It reveals not only the dominant role of electron tunneling in the transport process but also the invariance of the interfacial state as temperature varies. The tunnel barrier is most likely between the Nb:SrTiO$_3$ and the Q2DEG layer, and the depletion layer resistance seems to depend on the specific structural phase of the SrTiO$_3$ showing transitions at temperatures precisely where the SrTiO$_3$ phase transitions occur (Fig. 3(a)). Since the charge density in the forward bias case is high, variations in the charge transfer are not so obvious and so we need to look at the reverse bias case where the interface is depleted of carriers.

In the reverse bias case, the carriers in the Q2DEG channel are depleted with the channel showing an insulating behavior. Down to a temperature of about 120 K a variable range hopping (VRH) transport[17] is seen with $\exp(T^{-1/3})$ dependence for all bias values (Fig. 3(c)), characteristic of a 2D/3D VRH system (the temperature range 120−270 K is still too small to distinguish between the various dimensionalities since even a $\exp(T^{-1/4})$ gives a good fit). One would then

FIG. 2. (Color online) Current-voltage characteristics of Cu electrodes on (a) Nb-SrTiO$_3$ and (b) Q2DEG. (c) Semilogarithmic I-V characteristics measured in the temperature range from 270 to 5 K under positive bias. Solid lines are guides of linear part for fitting. (d) I-V curves obtained under negative bias.
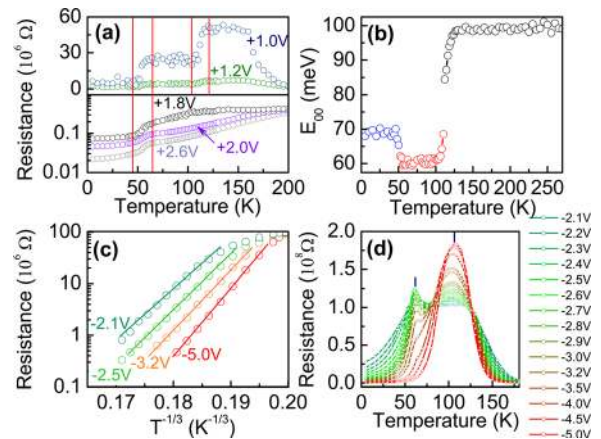

FIG. 3. (Color online) (a) Resistance versus temperature in forward bias as a function of applied voltage. (b) Temperature dependence of tunneling energy E_{00} from the slope of positive I-V curves. (C) VRH fitting in the insulator/semiconductor phase in high temperature from (d). (d) Resistance versus temperature in reverse bias as a function of applied voltage.

expect a temperature dependent transport through the defects presents at thermal equilibrium in $SrTiO_3$ to be responsible for the VRH. At 110 K, a clear departure from the VRH transport to a metallic one (insulator-metal transition) can be clearly observed (Fig. 3(d)), which can only be due to enhanced charge transfer to the $LaAlO_3$/$SrTiO_3$ interface. It is well known in published data (both ours and others)[18–20] that the mobility in the 2DEG enhances by more than an order of magnitude below 110 K. Coupled with the enhanced charge transfer induced by the phase transition, this will account for a metallic behavior below 110 K. Since the system is a VRH regime prior to the phase transition, the increase in mobility alone cannot account for this metallic behavior. The 55 K phase transition however has an opposing effect.

Comparing the carrier densities at 5 K for the forward and backward bias cases, a charge transfer ratio of 15:1 is estimated. This indicates that the amount of charge transfer at the 110 K insulator to metal transition is about 6%−7% of the observed charge transfer at the Q2DEG at 5 K under forward bias. Since the measured charge density at 5 K in the forward bias case is about $10^{13} cm^{-2}$, this accounts for a charge transfer of about $6-7 \times 10^{11}$ charges/cm^2. The actual numbers will slightly differ from these estimated numbers when the barrier effects are taken into account (the presence of barrier is evident in the reverse bias case as well because (e.g., at 150 K) the resistance is bias dependent).

We will now argue for the difference of the charge transfer at the interface to originate from the lattice mismatch strain at the $LaAlO_3$/$SrTiO_3$ interface. At room temperature there is likely to be a significant strain at the $LaAlO_3$/$SrTiO_3$ interface as $SrTiO_3$ is cubic while $LaAlO_3$ is orthorhombic. At 110 K, $SrTiO_3$ undergoes a cubic to tetragonal phase transition while $LaAlO_3$ remains unchanged. The c/a ratio of $SrTiO_3$ changes from 1 to 1.00056 during the phase transition.[21] This results in a reduced lattice mismatch between the overlayer $LaAlO_3$ and $SrTiO_3$ substrate. Recent paper by Park *et al.*[14] clearly showed that a 1% lattice mismatch could result in a charge transfer of $4 \times 10^{13} cm^{-2}$. Based on the above mismatch we would predict a charge transfer into the channel of about $5 \times 10^{12} cm^{-2}$, which is more than the observed charge transfer of $6-7 \times 10^{11}$ charges/cm^2. On the other hand at the 55 K phase transition the $SrTiO_3$ undergoes tetragonal to rhombohedral phase transition of reduced symmetry which may enhance the strain at the interface between $LaAlO_3$/$SrTiO_3$ (with c/a ratio is now 1.0004) which will increase the mismatch between the overlayer $LaAlO_3$ and the $SrTiO_3$ substrate. This represents an increase of the lattice mismatch of 0.01% which will reduce the charge transfer to the interface by 1.2×10^{12} charges/cm^2, accounting for the metal to insulator transition. Because we are dealing with a depleted channel we are able to see the small charge transfer in and out of the channel.

The effect of phase transition on the oxygen vacancies from quasi bulk $SrTiO_3$ surface also needs to be considered. When the channel is fully depleted the current arises from variable range hopping of residual charges to which oxygen vacancies can also contribute. However, the contribution to transport will decrease as one goes deeper from the interface. When the 110 K phase transition occurs the VRH behaviour changes to a metallic behaviour with a charge transfer of only $5 \times 10^{12} cm^{-2}$. The resistivity behavior changes from VRH to metallic (resistance decreasing with temperature). In order for this metallic behavior the local concentration of the carriers must approach $10^{20} cm^{-3}$ or more which will be very hard to realize from quasi-bulk surface of the $SrTiO_3$ via vacancies. On the other hand this strongly suggests charges confined to a 2D channel supporting our model.

Our experimental results, hence, clearly emphasize the interface strain between $SrTiO_3$ and $LaAlO_3$ to be responsible for modulating the charge transfer from $LaAlO_3$ to $SrTiO_3$. The measurement of the transport in the depleted channel of the rectifier has enabled us to measure the effect of interface strain on charge transfer at the $LaAlO_3$/$SrTiO_3$ interface, thereby shedding some light on some of the unresolved questions in the polar catastrophe model of the $LaAlO_3$/$SrTiO_3$ interface. Our results strongly suggest that the charge transfer to the Q2DEG layer is influenced by the interface strain, which accounts for the reduced charge transfer to the $LaAlO_3$/$SrTiO_3$ interface.

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